1. General

Type 316 stainless steels are metastable austenitic alloys that have molybdenum for improved corrosion resistance and high-temperature strength. Due to their high nickel and molybdenum content, this family of alloys has high stacking fault energy; a feature that promotes cross slip and is generally associated with superior hydrogen compatibility [1, 2].

Type 316 is sensitive to carbide precipitation on grain boundaries between approximately 773 K and 1073 K. A low-carbon grade, designated 316L, is used to moderate this sensitization; however, this may reduce stability since carbon is an austenite stabilizer. Carbides themselves are believed to have little, if any, effect on hydrogen susceptibility [3]; however, carbide precipitation in austenitic alloys has been linked to chromium depletion in adjacent areas. These chromium poor regions then become more prone to strain-induced martensitic transformations.

The role of martensite on hydrogen embrittlement in austenitic stainless steels has not been firmly established. Although generally viewed to be neither necessary nor sufficient to explain hydrogen susceptibility in austenitic stainless steels, α' martensite, in both sensitized and nonsensitized microstructures, is associated with lower resistance to hydrogen embrittlement. The trend for Fe-Cr-Ni stainless steels (300-series alloys) is that higher nickel concentration suppresses the martensitic transformation temperature and thus the strain-induced martensite [4-6].

1.1 Composition

Table Table 1.1.1 lists the composition ranges specified for one particular specification [7] and compositions of heats of 316 used to study hydrogen effects.

1.2 Other Designations

316L; UNS S31600, UNS S31603

2. Permeability and Solubility

Ref. [5] provides a summary of data for stainless steels.

3. Mechanical Properties in the Presence of Internal and External Hydrogen

3.1 Tensile properties

3.1.1 Smooth tensile properties

Room temperature tensile properties of 316 in gaseous hydrogen show no loss in ductility, Table 3.1.1.1. Some ductility loss was reported for material that was thermally charged, Table 3.1.1.1, however, the thermal charging cycle was in the sensitization range of this alloy and strain-induced martensite was reported when sensitized. In addition, this heat of 316, heat R84, had a relatively low nickel content (Table 1.1.1), presumably making it less resistant to the formation of strain-induced martensite. These data also differ in that the material was tested as thin sheet specimens which are thought to be more sensitive to hydrogen than standard bar specimens [8]. Effects of hydrogen on the flow stress of 316 are discussed in more detail in Refs. [8, 9].

Smooth bar tensile properties of 316 thermally charged from gaseous hydrogen and tested in air at several temperatures between 380 K and 200 K, Table 3.1.1.2, show relatively modest changes in strength and ductility due to hydrogen exposure [6]. Testing in 1 MPa hydrogen gas between room temperature and 80K, however, show a greater reduction in ductility (as measured by the ratio of reduction in area in hydrogen to helium) [3]. Both sets of data show a minimum in ductility loss due to hydrogen near 200 K. In addition to the difference in hydrogen source (internal versus external) in these two studies, the nickel content is substantially different in the two tested alloys. The lower nickel content of heat H98 may explain the greater susceptibility to hydrogen. This view must be expressed with caution, however, since the relative yield strengths of these alloys is not known, nor is the data sufficient to address differences between testing in the presence of internal or external hydrogen.

3.1.2. Notch tensile properties

Notched tensile specimens show no difference in properties when tested in 69 MPa helium or hydrogen, Table 3.1.2.1 [10].

3.2 Fracture mechanics

3.2.1 Fracture toughness

No known published data in gaseous hydrogen. Ref. [11] shows that both sensitization (see section 4.2) and cathodic charging with hydrogen lowered fracture toughness.

3.2.2 Threshold stress intensity

Low-strength austenitic microstructures (<700 MPa) have been shown to have high resistance to cracking in high-pressure hydrogen gas environments under static loads [12]. Data for 316 in two microstructural conditions are shown in Table 3.2.2.1.

3.3 Fatigue.

No known published data.

3.4 Creep.

No known published data.

4. Metallurgical considerations

4.1 Primary processing

Electroslag refining (ESR) of type 316 stainless steel improved the fracture toughness of cathodically charged material to values greater than determined for unrefined, annealed 316 of nominally the same composition [11]. Higher annealing temperatures were also found in this study to improve the fracture toughness of charged and sensitized materials.

4.2 Heat treatment

Type 316 stainless steel shows a larger susceptibility to hydrogen embrittlement in smooth tensile bars when sensitized (973 K for 24 h) compared to solution-annealed microstructures [3]. Solution-annealed microstructures (of both 304 and 316 stainless steels) featured strain-induced α’ martensite distributed through the grain structure and transgranular fracture, while sensitized microstructures featured α' martensite preferentially along grain boundaries and intergranular failure [3]. The transition from transgranular failure to intergranular fracture is accompanied by loss in ductility. There is no direct evidence that the martensite contributes to fracture, however, it is speculated that α' martensite may facilitate hydrogen accumulation at the crack tip by enhancing hydrogen mobility [3], or perhaps by acting as trapping sites for hydrogen.

4.3 Properties of welds

No known published data. Laser Engineered Net Shaping (LENS™) is a process that has features analogous to fusion welding processes: powders are melted with a laser, solidified on a substrate and built-up in subsequent passes. The ductility of smooth tensile bars machined from LENS™-fabricated 316 materials have been reported in Ref. [13]. The loss of ductility due to thermal charging with hydrogen (138 MPa gaseous hydrogen at 300°C for 10 days) was found to be greater in LENS™ compared to a wrought 316 and to data from Table 3.1.1.1. Fracture was localized near interlayer boundaries in hydrogen charged specimens with secondary cracking near interpass boundaries normal to the fracture surface.

5. References

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Table 1.1.1. Composition of several heats of 316 stainless steel used to study hydrogen effects as well as limits for one variety of 316 and one variety of 316L.

Heat	Cr	Ni	Mn	Mo	Si	C	N		Ref.
AMS 5648K	16.00 18.00	10.00 14.00	1.25 2.00	2.00 3.00	1.00 max	0.08 max	---	0.030 max S; 0.040 max P; 1.00 max Cu	[7]
AMS 5653F	16.00 18.00	10.00 14.00	1.25 2.00	2.00 3.00	1.00 max	0.03 max	---	0.030 max S; 0.040 max P; 1.00 max Cu	[14]
O76	17.41	13.51	1.56	2.53	0.71	0.061	---		[2]
P81	17.5	13.5	0.06	2.5	0.17	0.05	0.07	<0.02 Ti ; 0.02 Co; <0.01 Nb	[12]
R84	17.7	10.2	1.4	1.6	0.6	0.029	---	Designated 316L	[8]
H98	17.10	10.05	0.66	2.02	0.48	0.040	---	0.002 S; 0.010 P	[3]

Table 3.1.1.1. Tensile properties of 316 stainless steel tested at room temperature in hydrogen gas or thermally precharged in gaseous hydrogen and tested in air.

Material	Test environment	Thermal precharging	S_y (MPa)	S_u (MPa)	El_u (%)	El_t (%)	RA (%)	Ref.
Not specified	69MPa He	None	214	496	---	68	78	[1, 15]
	69MPa H_2	None	214	524	---	72	77	
Cold drawn	69MPa He	None	441	648	---	59	72	[10]
	69MPa H_2	None	---	683	---	56	75	
Annealed plate, heat O76	Air	None	262	579	---	68	78	[2]
	69MPa H_2	None	221	524	---	72	77	
Sensitized thin sheet, heat R84	Air	(1) – Ar	327*	685	62	63	---	[8]
	Air	(1) – H_2	331*	691	43	51	---	

(1) 0.5 MPa hydrogen or argon gas, 873K, 170 hours: measured concentration of ~6 wppm hydrogen (300-325 appm)
* stress at 0.2% strain

Table 3.1.1.2. Effect of internal hydrogen (thermal charging in high-pressure hydrogen gas) on tensile properties of 316 at low temperatures tested in air, from Ref. [6]; composition and metallurgical condition not given.

Test temperature (K)	Thermal precharging	Flow stress* (MPa)	Ultimate Stress† (MPa)	El_u (%)	El_t (%)	RA (%)
380	None	810	830	7	20	80
	(1)	880	930	11	22	70
273	None	890	1040	21	33	77
	(1)	990	1160	20	32	68
250	None	900	1150	27	40	78
	(1)	1030	1280	24	35	66
200	None	960	1210	24	43	79
	(1)	1100	1410	26	37	65

(1) 69 MPa hydrogen gas, 620 K, 3 weeks
* true stress at 5% strain
† true stress at maximum load

Table 3.1.2.1. Notch tensile properties of 316 stainless steel tested in hydrogen gas at room temperature. The included angle of the notch was 60˚ with an original notch diameter of 3.81 mm (0.15 inch) in a gage diameter of 7.77 mm (0.306 inch). The notch root radius was 0.024 mm (0.00095 inch) and the displacement rate was approximately 4 x10^{-4} mm/s [10].

Material	Test environment	Thermal precharging	S_y † (MPa)	σ_s (MPa)	RA (%)	Ref.
Cold drawn	69MPa He	None	441	1110	18	[10]
	69MPa H_2	None	---	1110	19	

† yield strength of smooth tensile bar

Table 3.2.3.1. Threshold stress intensity for 316 (heat P81 in table 1.1.1) in high-pressure hydrogen gas from Ref. [12] (data also reported in Ref. [16]).

Condition	S_y (MPa)	RA (%)	Threshold Stress Intensity (MPa $m^{1/2}$)	
			100 MPa H_2	200 MPa H_2
HERF 840˚C, WQ	689	65	NCP 132	NCP 132
WR 600˚C, WQ	903	70	---	99†

† did not satisfy plane strain requirements for analysis of stress intensity
HERF = high-energy rate forging, WQ = water quenched, WR = warm-rolled
NCP = no crack propagation at given stress intensity